

(12) Invention Description To Accompany Claim

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(72) Alekseev V.A., Bilibin S.V., Molokhina L.A., Oparin Yu.Ya., Ryabikova G.A., Filin S.A.

(71) Separate research division for solar and precision optics under science and production association GP "Astrofizika"

(54) RETRO-REFLECTING MATERIAL

(57) This invention, 'Retro-reflecting material', corresponds to the fabrication of retro-reflecting materials containing transparent microspheres and functioning as reflectors, that under pulsed irradiation reflect light of predefined color that is stable in time and under any weather conditions, and that can be used in technical means for road traffic control, such as road signs, direction signs, screens, road markings, car license plates, special elements for detection in the dark, credit cards, warning signs, etc., as well as for achieving lighting effects in the cinema, on stage, at discotheques, including those cases in which no light sources should be visible. The technical result of this invention is that the light flux reflected under pulsed irradiation becomes more stable in time, and also that the retro-reflecting material becomes brighter and more reliable. According to the first variant, the time-stability of reflected light flux under pulsed irradiation and the brightness and reliability of the retro-reflecting material are achieved as follows. The retro-reflecting material contains i) transparent microspheres fixed on a support by a solid solution of fluorescent color-carrying particles in a binder layer and ii) reflecting elements; a protective layer of transparent film-forming material fixed by a binder layer is introduced in the retro-reflecting material; the support features a mirror-type metallized reflective surface with a monolayer of microspheres fixed on it; a solid solution (0.4-20.5% vol.) of luminophore particles with at least one luminescence color in a layer of a binder or a film-forming material is used as the solution. According to the second variant, the technical result is achieved as follows. The retro-reflecting material contains i) transparent microspheres fixed on a support by a binder layer; ii) reflecting elements; and iii) a fluorescent color-carrying compound; a luminescent film-type light filter fixed on the binder layer is introduced in the retro-reflecting material; the support has a mirror-type metallized reflective surface with a monolayer of microspheres fixed on it. The technical result according to the third variant is achieved as follows. The retro-reflecting material contains i) transparent microspheres fixed on a support by a binder layer; ii) reflecting elements; and iii) fluorescent color-carrying particles; a protective layer of transparent film-forming material is introduced in the retro-reflecting material; luminophore particles with at least one luminescence color and with transparency no lower than 16.0% are deposited on the back surface of that layer, and the support is made as a mirror-type metallized reflective surface with a monolayer of microspheres fixed on it.

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RETRO-REFLECTING MATERIAL

The proposed invention corresponds to the fabrication of retro-reflecting materials containing transparent microspheres and functioning as reflectors that, when exposed to pulsed irradiation, reflect light of predefined color that is stable in time and under any weather conditions, and that can be used in technical means intended for road traffic control, such as road signs, direction signs, screens, road markings, car license plates, special elements for detection in the dark, credit cards, warning signs, etc., as well as for lighting effects in the cinema, on stage, at discotheques, including those cases in which no light sources should be visible.

At present, the problem of fabricating retro-reflecting materials that work under pulsed irradiation has become rather urgent due to the necessity for obtaining soft retro-reflection towards the source with predefined color and time-stability, particularly under periodic irradiation, under various light conditions, *e.g.*, on stage, at discotheques, in the cinema, etc., as well as for detecting objects in the dark without exposing the irradiation source. With currently existing retro-reflecting materials, the reflected light flux of pulsed sources is discontinuous or its brightness is highly non-uniform between the pulses, or it is technically difficult to achieve color effects in reflected light.

A known retro-reflecting material (USA Patent No. 3758193, Int. Cl. G02B5/128, NCI 350/105, 1977) consists of a support with a reflective surface, a monolayer of transparent microspheres fixed between a protective layer of transparent film-forming material with a flat outer surface and a reflective surface; they are fixed by means of a binder layer of transparent film-forming material consisting of a solid solution of pigment particles of at least one color at a volume concentration of the particles between 0.5 and 20.0% vol.

However, light flux from a pulsed irradiation source reflected from the known retro-reflecting material is unstable in time. It does not provide retro-reflection that would be soft, stable in time and have a predefined color under periodic irradiation of the material; moreover, the known material requires a source of visible light, which is sometimes undesirable.

The most similar technical solution (prototype) comprises a retro-reflecting material featuring a support with a coating from a reflective color-carrying composition that consists of a binder, reflective color-carrying particles with diffuse reflection mainly made of metal oxides and salts, transparent microspheres, and fluorescent organic color-carrying particles (USA Patent No. 3030870, Int. Cl. G02B5/128, NCI 305/105, 1962).

However, the light flux from a pulsed irradiation source reflected from the known retro-reflecting material is highly unstable or discontinuous in time because fluorescent organic colored particles,

that are used in the known technical solution, display short-time luminescence and hence short-time phosphor persistence after an irradiation pulse. Moreover, the use of just one type of such particles does not allow one to obtain a required multi-color reflection of the light flux from such retro-reflecting material. The composition with fluorescent particles covering the support is unstable and is quickly decomposed due to the absence of a protective coating, or quickly loses its fluorescent properties due to the use of nondurable and unstable fluorescent organic particles that lose their fluorescent properties in a few weeks. The known retro-reflecting material also has low luminosity of the reflected light flux because diffusive reflecting particles based on metal oxides and salts are used to provide reflection. Furthermore, the production of such retro-reflecting material is complicated due to difficulties involved in obtaining and applying a complex multicomponent composition.

The new technical result achieved by the proposed invention is that the light flux reflected under pulsed irradiation becomes more uniform in time, and also that the retro-reflecting material becomes more luminous and reliable.

According to the first variant, the new technical result is achieved as follows. The known retro-reflecting material contains i) transparent microspheres fixed on a support by a solid solution of fluorescent color-carrying particles in a binder layer and ii) reflecting elements. Unlike the prototype, a protective layer of transparent film-forming material fixed by a binder layer is introduced in the retro-reflecting material; the support is fabricated with a mirror-type metallized reflective surface and with a monolayer of microspheres fixed on the latter; a solid solution (0.4-20.5% vol.) of luminophore particles with at least one luminescence color in a binder or in a film-former layer is used as the solution.

According to the second variant, the technical result is achieved as follows. The known retro-reflecting material contains i) transparent microspheres fixed on a support by a binder layer; ii) reflecting elements; and iii) a fluorescent color-carrying compound. As opposed to the prototype, a luminescent film-type light filter fixed on the binder layer is introduced in the retro-reflecting material; the support is made as a mirror-type metallized reflective surface with a monolayer of microspheres fixed on it.

According to the third variant, the technical result is achieved as follows. The known retro-reflecting material contains i) transparent microspheres fixed on a support by a binder layer; ii) reflecting elements; and iii) a fluorescent color-carrying particles. As opposed to the prototype, a protective layer of transparent film-forming material is introduced in the retro-reflecting material; luminophore particles with at least one luminescence color and with transparency no lower than

16.0% are deposited on the back surface of that layer, and the support is made as a mirror-type metallized reflective surface with a monolayer of microspheres fixed on it.

Figures 1 and 2 (the first variant), Figure 3 (the second variant), and Figure 4 (the third variant) demonstrate the scheme of the retro-reflecting material.

The retro-reflecting material corresponding to the first variant contains a monolayer of transparent microspheres 1 fixed on a mirror-type metallized surface 2 of the support 3 by a binder layer 4, and a transparent protective layer of a film-forming material 5 bound to the latter 4, wherein the binder layer 4 or the film-forming material layer 5 is a solid solution (0.4-20.5% vol.) of luminophore particles with at least one luminescence color 6 in these materials.

The retro-reflecting material corresponding to the second variant (Fig. 3) contains a monolayer of transparent microspheres 1 fixed on a mirror-type metallized reflective surface 2 of the support 3 in a binder layer 4, and a luminescent film-type light filter 7 bound to the latter.

The retro-reflecting material corresponding to the third variant (Fig. 4) contains a monolayer of transparent microspheres 1 fixed on a mirror-type metallized reflective surface 2 of the support 3 in a binder layer 4, and a transparent protective layer of a film-forming material 5 bound to the latter 4; luminophore particles with at least one luminescence color 8 and with transparency no lower than 16% are deposited on the back surface of that layer.

The retro-reflecting material is fabricated as described below.

According to the first variant, a mirror-type metallized reflective coating 2, e.g., aluminum, is deposited onto a support 3, e.g., a polymer (polyethylene, lavsan, etc.), using any standard method, for example, by sputter-deposition in a vacuum set-up.

After that, a solid solution of luminophore particles 6, e.g., $0.5 \text{ ZnS} \cdot 0.5 \text{ CdS} \cdot 3 \cdot 10^{-4} \text{ Ag} \cdot 3 \cdot 10^{-6} \text{ Ni}$ (particle size $0.5\text{--}5.0 \text{ }\mu\text{m}$) in a binder layer 4 (Fig. 1) or in a transparent protective layer of a film-forming material 5 (Fig. 2) is prepared. The use of luminophores with particle size less than $0.5 \text{ }\mu\text{m}$ decreases abruptly the light intensity of the retro-reflecting material, whereas if the particles are larger than $5.0 \text{ }\mu\text{m}$, the luminophore sensitivity and resolution are impaired.

To prepare the solution, luminophore particles 6 are added to achieve a volume concentration of 0.4-20.5% vol. ($0.4\text{--}205 \text{ cm}^3/\text{l}$) in a binder 4 (Fig. 1) or in a film-forming material 5 (Fig. 2), e.g., in acrylic lacquer AK-545 (STP6-10-500-31-87), in the "Metafont" material produced by the "LIT" enterprise (based at Pereyaslavl-Zalessky), or in the GIPK-2214 adhesive (TU 6-05-251-64-87, TU 6-05-251-49-88), with adequate mixing. The film-forming material 5 can also be made of polyethylene, lavsan, polystyrene, etc.

If the volume concentration of luminophore particles 5 is higher than 20.5% vol., the transparency of the binder 4 decreases abruptly, and the latter ceases to pass light to the mirror-type surface 2. At volume concentrations of luminophore particles 5 below 0.4% vol., the uniformity of screen light emission decreased abruptly during the time periods between the irradiation source pulses. The optimum volume concentration of luminophore particles 2 is 1-10% vol.

After that, the prepared solution of luminophore particles 6 in the binder 4 is applied onto the mirror-type metallized surface 2 (Fig. 1) and then microspheres 1 with diameters in the range 2.0-1000.0 μm are applied. The microspheres can be made of glass (Latvian Republic TU 024-80), polystyrene, quartz, polymethyl acrylate, etc., with refractive index in the range 1.4-2.0; they are applied from a sieve or by spraying onto the binder layer 4. If a sieve is used, the applied microspheres 1 belong to a single fraction and have similar sizes.

Thereafter, the microspheres 1 are immersed into the layer of the solid solution of luminophore particles 6 in the binder 4, *e.g.*, by rolling the retro-reflecting material with microspheres 1 between rolls until the microspheres have been immersed, *e.g.*, down to the mirror-type metallized reflective surface 2.

The size of microspheres 1, that is, the diameter range of 2.0-1000.0 μm , is limited by the following factors. Technological and geometrical difficulties are encountered in the fabrication of microspheres smaller than 2.0 μm , whereas if the microspheres are larger than 1000.0 μm , light reflection from them does not resemble a whole (non-discrete) body for normal human vision.

Thereafter, a transparent protective layer of a film-forming material 5 is fixed on the binder layer 4 containing luminophore particles by applying a layer of AK-545 varnish, GIPK-2214 adhesive, polyethylene or lavsan film, etc.

The following procedure is used for a solid solution of particles 6 in a layer of film-forming material 5. The solid solution of luminophore particles 6 in a film-forming material 5, *e.g.*, AK-545 varnish, GIPK-2214 adhesive, etc., obtained similarly to the procedure described above, is bound to a layer of pure binder 4 with a monolayer of microspheres 1 fixed in it and installed on a mirror-type metallized reflective surface 2 (Fig. 2).

According to the second variant, a luminescent film-type light filter 7 is bound to a layer of pure binder 4 with a monolayer of microspheres 1 installed on the mirror-type metallized reflective surface 2 of support 3, which constitute a part of a retro-reflecting material obtained similarly to the procedure described above (Fig. 3).

As an example, a homogeneous film-type light filter (green) can be used as the luminescent film-type light filter. It consists of methyl methacrylate, dibutyl phthalate, 5,8-dihydroxy-1,4-(4,4')-

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methylphenylaminoanthraquinone (oil-soluble green Ж), 2-(1-phenyl-3-methylpyrazolone-5)azometha-xylene (oil-soluble yellow Ж), lauric acid, and dinitrideazoisobutyric acid; it has the following spectral and color characteristics:

Wavelength of maximum light transmittance – 532 nm

Light transmittance in the maximum – 43%

Chromaticity coordinates in the system X0.32 Y0.65

X, Y, Z for A-type source

Other film-type light filters, *e.g.*, those described in Author's Certificates Nos 763833, 611075, *etc.*, can also be used.

The use of fluorescent film-type filters with homogeneous compositions and predefined transparency and luminescence color provides the possibility of using standard industrial film-type materials for manufacturing retro-reflecting materials. There is no need to make such industrial materials as they are available commercially; this simplifies considerably the production of retro-reflecting materials with luminescent properties working under pulsed irradiation.

According to the third variant (Fig. 4), a layer of pure binder 4 with a monolayer of microspheres 1 installed on the mirror-type metallized reflective surface 2 of support 3 (which together constitute a part of a retro-reflecting material obtained using the above procedure) is covered with a protective transparent layer of film-forming material 5, *e.g.*, AK-545 varnish, GIPK adhesive, polyethylene, lavsan, *etc.*, the back surface of which has been pre-coated with luminophore particles 6 with at least one luminescence color to a thickness of 0.1-1.0 μm , *e.g.*, by deposition in electrostatic (gravitation) field or by vacuum sputtering, so as to provide the transparency of deposited luminophore 6 no less than 16.0%.

The retro-reflecting material works as described below.

When a retro-reflecting material obtained according to the first variant is irradiated by a pulsed source, *e.g.*, a car flasher, a pulse CO_2 laser, *etc.*, irradiation freely penetrates its working surface to reach the layer with fluorescent properties, that is, a solid solution of luminophore particles 6 in a binder layer 4 (Fig. 1) or in a film-forming material (Fig. 2). The luminophore particles 6 are irradiated, *e.g.*, with the red monochromatic spectral line of a pulse CO_2 laser (pulse duration 3 μs ; pulse interval 1 s). The luminophore particles start to emit light that decays gradually after a pulse has ended; the post-luminescence duration provides a uniform luminosity of the material between the pulse periods.

A fraction of the light flux that has passed through the solid solution of luminophore particles 6 in the binder 4 (Fig. 1) or in the film-forming material and then through the transparent binder layer 4

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(Fig. 2) falls on the monolayer of microspheres 1; the light is refracted in the latter and then reflected from them and also from the mirror-type metallized reflective surface 2 of support 3, and then again hits the luminophore particles 6 in the binder layer 4 (Fig. 1) or freely passes through the transparent binder layer 4, and again hits the luminophore particles 6 in the layer of the film-forming material (Fig. 2), thus also ensuring the post-luminescence of the retro-reflecting material between the irradiation pulse periods of the light source.

The remaining fraction of the light flux that has been reflected from microspheres 1 and the mirror-type metallized reflective surface 2 and has not been absorbed by luminophore particles 6 is retro-reflected to the irradiation source.

This creates soft comfortable conditions for viewing both the retro-reflecting material (the information it carries), whose luminosity is rather stable between the irradiation pulses, and the retro-reflected light flux re-reflected by the microspheres 1 and the mirror-type metallized reflective surface 2.

When the working surface of a retro-reflecting material obtained according to the second variant is irradiated by a pulsed source similarly to the procedure described above, the light flux acts on the luminescent film-type light filter 7 (Fig. 3). As a result, the light filter 7 starts to emit light that decays gradually once the pulse has ended; this provides a uniform luminosity of the material between the pulse periods.

A fraction of the light flux that has passed through the light filter 7 is reflected from the optical system consisting of microspheres 1 and the mirror-type metallized reflective surface 2, retro-reflected to the light filter 7 similarly to the situation shown in Fig. 2, and again acts on the light filter, making it luminesce and also provide the post-luminescence of the retro-reflecting material between the pulse periods of the light source.

The remaining fraction of the light flux that has been reflected from microspheres 1 and the mirror-type metallized reflective surface 2 and has not been absorbed by the light filter 7 is retro-reflected to the irradiation source.

When the working surface of a retro-reflecting material obtained according to the third variant is irradiated by a pulsed source (Fig. 4), the light flux freely passes the protective transparent layer of the film-forming material 5 and reaches the layer of luminophore particles 8 deposited on its back surface. As a result, they are irradiated and start to emit light that decays gradually after a pulse has ended; the post-luminescence duration provides a uniform luminosity of the material between the pulse periods.

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A fraction of the light flux (no lower than 16.0%) that has passed through the applied layer of luminophore particles 6 falls on the optical surface of the system consisting of microspheres 1 and the mirror-type metallized reflective surface 2; the light is reflected from this system, again reaches (in the way described above) the layer of luminophore particles 8 and acts on these particles, making them luminous and also provide the post-luminescence of the retro-reflecting material between the pulse periods of the light source.

The remaining fraction of the light flux that has been reflected from the optical surface of the system comprising microspheres 1 and the mirror-type metallized reflective surface 2 and has not been absorbed by the layer of luminophore particles 8 will be retro-reflected back to the irradiation source.

In the technical solution proposed, the use of luminophore particles [organic and inorganic compounds that can emit light (luminesce) when exposed to external factors (light)], instead of fluorescent organic color-carrying particles (characterized by short-lived luminescence which decays quickly after irradiation has stopped) used in the prototype, expands the scope of application of luminescent compounds (both organic and inorganic) and makes it possible to prolong their post-luminescence (long-duration luminescence). The combination of these factors provides the time-uniform light emission of the retro-reflecting material between the pulses.

The double excitation of luminescent layers (solid solutions of binder 4, film-forming material 5 or layer of luminophore particles 8) by light flux passing "forward" and by the retro-reflected flux also makes it possible to prolong the post-luminescence in comparison with the prototype.

Luminophore particles 5 ensure both continuous luminescence of the screen material under pulsed irradiation and the required color range of light which the material emits. For example, the ZnS-AgCu luminophore provides a blue radiation band; ZnS-Ag, Au provides a yellowish-green band; copper-activated zinc-cadmium sulfide (Zn,Cd)S-Cu provides a green band; europium-activated yttrium oxysulfide $Y_2O_3 \cdot Eu$ provides a red band. A K3-2 luminophore mixture can be used; depending on the ratio of its two components, it provides reddish-orange, orange-yellow, or greenish-yellow color of luminescence. The luminophore particles 5 can contain more components, depending on the required luminescence color range.

The color of irradiation of a material containing luminophore particles 5 can be either different from the luminescence color (red from a CO_2 laser and green from a luminophore) or invisible, provided that UV or IR irradiation is used while bismuth diethyldithiocarbamate or $0.5ZnS \cdot 0.5CdS \cdot 3 \cdot 10^{-4} Ag \cdot 3 \cdot 10^{-6} Ni$, respectively, is used as luminophore particles 5. The parameters of the screen obtained by this method were as follows: sensitivity threshold $1.3 \cdot 10^{-3} W/cm^2$, resolution capability

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5-6 lines/mm at $I_{\text{peak}} = 1.3 \cdot 10^{-3} \text{ W/cm}^2$ and 12^{-3} lines/mm at $I_{\text{peak}} = 2.0 \cdot 10^{-2} \text{ W/cm}^2$; the dynamic range is 20.

The protective coating in a retro-reflecting material (film-forming material 5 or light filter 7) increases its service reliability by at least 15% with respect to premature failure due to adverse climatic factors and mechanical damage in service; the working surfaces of such protective films can be cleaned from contamination on a regular basis or replaced, thus increasing the luminosity of the retro-reflecting material and prolonging its operational life.

The transparency of the layer of luminophore particles 8 deposited on the back side of the protective layer of film-forming material 5 (Fig. 4) should not be lower than 16%, which is required both for ensuring the post-luminescence of the retro-reflecting material between the irradiation pulses and for providing efficient retro-reflection of the incident light flux with sufficient brightness for all the main colors of the visible range. For example, for the red and blue components, their reflection by a retro-reflecting material with brightness less than 20% of the white light flux prevents their visualization by normal human vision with sufficient contrast and color perception.

Beside a laser, the following pulsed irradiation sources can be used: electric light sources (e.g., a projector); sources of UV, IR and mixed irradiation.

Handbooks list the main luminophores and the corresponding irradiation wavelengths that provide a required luminescence spectrum of a luminophore or a group of luminophores. See, e.g., the following handbooks: J. De Ment, "Fluorochemistry", p. 35, Table 7, published by Chemical Publishing Company, 1945; and "The Luminescent Dyestuff Index", 1945, etc.

Either a single source or different sources with different wavelengths can be used to irradiate the optical retro-reflecting system comprising microspheres 1 and a mirror-type metallized reflective surface 2 and the luminophore particles 6, 8. For example, irradiation of e.g. the $\text{Y}_2\text{O}_2\text{S-Eu}$ luminophore by a UV source with a wavelength of $\sim 3500 \text{ nm}$ giving red luminescence, simultaneously with irradiation by a CO_2 -laser giving red monochromatic light, gives the retro-reflected light with the same color as the luminescence. On the other hand, the luminescence color and the color of the retro-reflected light can be different (iridescent), depending on the wavelength(s) of the irradiation source(s); this can provide color effects on stage, at discotheques, in the cinema, etc., if the luminescence color differs from the irradiation color.

As shown by results of the tests carried out on a "NIIAVTOpribor" according to the standard international procedure, the time-uniformity of the light flux reflected from the retro-reflecting material exposed to pulsed irradiation with the specified parameters is not worse than 30%, whereas for the prototype, the similar uniformity depends on the pulse duration and fluorescent particles

used and is not better than 95% (the difference between the maximum and minimum values), that is, the pulse behavior is practically retained.

The luminance factor of retro-reflecting materials increases to $46.9 \text{ cd/lm}\cdot\text{m}^2$ in comparison with $20.1 \text{ cd/lm}\cdot\text{m}^2$ (prototype) for the red spectrum line owing to the use of a reflective optical system comprising a monolayer of microspheres 1 installed on a mirror-type metallized reflective surface 2, in comparison with a system of microspheres 1 randomly located at different layers, whose diffuse reflecting properties are due to the light from randomly distributed color-carrying particles of oxides and salts of various metals, such as TiO_2 , FeO , CaSO_4 , BaSO_4 , etc. (prototype).

Based on the above, the new technical results achieved are as follows.

1. An increase (by up to 30%) in the time-uniformity of light reflected from a retro-reflecting material and of light emission by the latter under pulsed irradiation due to the use of a solid solution of luminophore particles in a binder or a film-forming material, or in a deposited layer, with the post-luminescence duration matching the length of pulses that irradiate the retro-reflecting material.
2. An increase (at least twofold) in the luminosity of retro-reflecting materials due to the use of a more efficient optical reflective system comprising a monolayer of microspheres installed on a mirror-type metallized reflective surface.
3. An increase in the reliability of the retro-reflecting material at least by 15% due to preservation of its retro-reflecting layer by means of a protective layer.
4. Simplification of the manufacturing technology by using standard film-type light filters with luminescent properties.
5. The possibility of using sources with various spectra (from IR to UV), including pulsed and monochromatic ones, for irradiation of retro-reflecting material, while ensuring that it emits light with a required color range due to the use of the appropriate luminophore particles and their combinations.
6. The possibility of using invisible (or visible + invisible) irradiation from a source in order to obtain colored reflection from a retro-reflecting material.

As of now, the proposed retro-reflecting material has been tested at NPO GP "Astrofizika"; design documentation has been issued, and samples of the proposed retro-reflecting material have been fabricated on the basis of that documentation.

V.A.Alekseev

Director of OP "SOLTO" at NPO GP "Astrofizika"

Claims:

1. What is claimed is a retro-reflecting material comprising transparent microspheres fixed on a support by means of a solid solution of fluorescent color-carrying particles in a binder layer, and reflective elements, wherein the retro-reflecting material contains a transparent protective layer of a film-forming material fixed on the binder layer, the support features a mirror-type metallized reflective surface with a monolayer of microspheres fixed on the latter, and the solid solution of luminophore particles with at least one luminescence color in a binder or film-forming material layer with a volume concentration of 0.4-20.5% is used as the solution.
2. What is claimed is a retro-reflecting material comprising transparent microspheres fixed on a support in a binder layer, reflective elements and a fluorescent color-carrying compound, wherein the retro-reflecting material contains a luminescent film-type light filter fixed on the binder layer, and the support features a mirror-type metallized reflective surface with a monolayer of microspheres fixed on the latter.
3. What is claimed is a retro-reflecting material comprising transparent microspheres fixed on a support in a binder layer, reflective elements and fluorescent color-carrying particles, wherein the retro-reflecting material contains a protective transparent layer of a film-forming material with luminophore particles deposited on the back surface of the said layer, the luminophore particles having at least one luminescence color and transparency of at least 16.0% in the visible spectrum, and the support has a mirror-type metallized reflective surface with a monolayer of microspheres fixed on the latter.

V.A.Alekseev

Director of OP "SOLTO" at NPO GP "Astrofizika"